

Electronic Structure Calculation of the Structures and Energies of the Three Pure Polymorphic Forms of Crystalline HMX

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The molecular structures and energetic stabilities of the three pure polymorphic forms of crystalline HMX were calculated using a first-principles electronic-structure method. The computations were performed using the local density approximation in conjunction with localized “fireball” orbitals and a minimal basis set. Optimized cell parameters and molecular geometries were obtained, subject only to preservation of the experimental lattice angles and relative lattice lengths. The latter constraint was removed in some calculations for β -HMX. Within these constraints, the comparison between theory and experiment is found to be good. The structures, relative energies of the polymorphs, and bulk moduli are in general agreement with the available experimental data.

I. Introduction

Plastic-bonded explosives (PBXs) are highly filled (ca. 90% w/w filler) composite materials comprising grains of a high-explosive (HE) material held together by a polymeric binder. There is a need to better understand the physical, chemical, and mechanical behaviors of the constituents of PBX formulations, as well as the interactions between them, from fundamental theoretical principles. Among the quantities of interest are thermodynamic stabilities, reaction kinetics, equilibrium transport coefficients, mechanical moduli, and interfacial properties. These properties are needed, generally as a function of stress state and temperature, for the development of improved micromechanics models which represent the composite at the level of grains and binder. Improved micromechanics models are needed to describe the response of PBXs to dynamic stress and/or thermal loading to yield information from which constitutive laws for use in continuum modeling approaches can be formulated and/or parameterized.

The compound octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) is the energetic constituent in several high-performance PBX formulations.¹ It exists in three pure crystalline forms, denoted as α -, β -, and δ -HMX. Figure 1 contains a three-dimensional rendering of the unit cell for β -HMX, which is the thermodynamically stable form under ambient conditions. However, post-mortem analysis² of samples recovered from safety experiments involving low-velocity projectile impacts on the HMX-based PBX-9501³ has revealed formation of δ -HMX in the vicinity of damaged regions within the material. It is also known that a layer of δ -HMX is formed at the solid–melt interphase in deflagrating HMX. These observations present a safety concern since δ -HMX is considerably more sensitive than β -HMX.

In this paper we report quantum mechanical studies of the crystal structures of α -, β - and δ -HMX. Previous calculations using a quantum mechanical approach for these and a similar

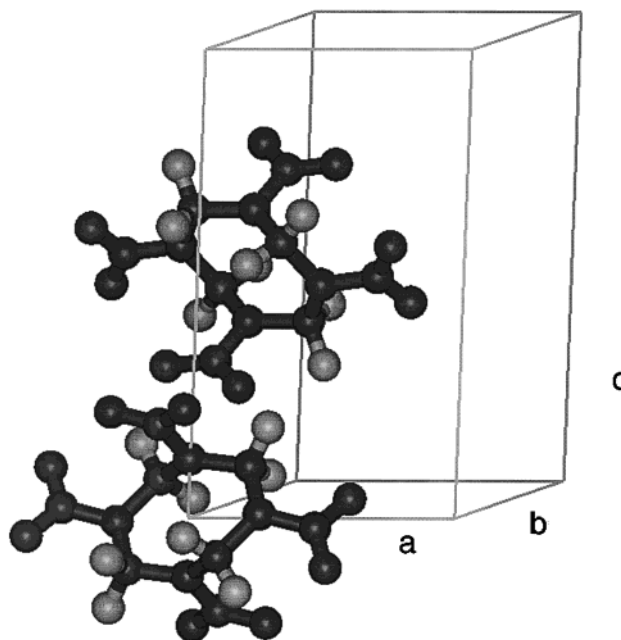


Figure 1. Unit cell of β -HMX.

HE material (RDX) have been reported,^{4–9} but none of this previous work has examined such materials in the condensed phase. Although gas-phase calculations have been performed on various HE materials, such calculations fail to account for important condensed-phase effects. The purpose of the present work is to assess the usefulness of a density functional approach for computing the condensed-phase properties of HMX, and represents a necessary step in a progression toward first-principles predictions of some of the physical and chemical properties mentioned previously. The criteria by which we judge our results are the comparison of predicted and measured crystal structures and relative energetics of the polymorphs to experiment, and a comparison of the measured and calculated bulk modulus and its pressure derivative for β -HMX.

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The sections of this paper are organized as follows: The computational methods are described in section II. Section III contains a comparison among the results for the three polymorphs and discussion of the important points. Finally, section IV contains concluding remarks.

II. Computational Methods

The electronic-structure method used to perform the calculations described in this work is based on norm-conserving pseudopotentials^{10,11} and the local density approximation (LDA) limit of DFT, but uses the Harris functional¹² and a minimal nonorthogonal local-orbital basis of slightly excited orbitals.^{13,14} The LDA limit is a reasonable approximation for the HMX polymorphs calculated here because HMX forms a molecular crystal largely via electrostatic interactions rather than hydrogen-bonding interactions. By contrast, this approach would not be suitable for the HE TATB (1,3,5-triamino-2,4,6-trinitrobenzene) which exhibits both strong inter- and intramolecular hydrogen bonding.

The electronic eigenstates are expanded as a linear combination of pseudoatomic orbitals within a localized sp^3 basis for oxygen, nitrogen, and carbon, and an s basis for hydrogen. These localized pseudoatomic orbitals, which we refer to as “fireballs”, are slightly excited due to the boundary condition that they vanish at some radius r_c ($\psi_{\text{fireball}}^{\text{atomic}}(r)|_{r=r_c} = 0$) instead of the “atomic” boundary condition that they vanish at infinity. The cutoffs (2.9, 3.8, 3.6, and 3.4 Å for H, C, N, and O, respectively) are chosen in a way that preserves the relative ionization energies and relative atomic sizes for each species. We accomplish this by noting that the atomic energies of the atoms all seem to follow a near “universal” behavior as a function of r_c .¹⁴ The fireball boundary condition has the effect of limiting the range of coupling matrix elements between orbitals on different atoms, which creates a sparse Hamiltonian matrix.

Because the Harris functional is inherently nonself-consistent, its applications are somewhat limited to systems which do not exhibit a significant difference in the electronegativity of their constituents, such as in the case of HMX. As a result, a recent extension of the Fireball method is used to self-consistently evaluate the atomic densities, allowing one to deal with systems which exhibit a significant charge transfer between atoms.¹⁵ This self-consistency method maintains the short-range nonorthogonal local-orbital basis, real-space analysis (except in the simple Ewald summation), and there are no integrals involving four or more centers. This first-principles-derived tight-binding-like methodology has been applied to many complicated systems and has proven to be computationally fast and quantitatively accurate.¹⁴

Within this electronic structure method, forces for each atom are determined using a variation of the Hellmann–Feynman Theorem.¹⁶ The derivatives taken to determine the forces are of the matrix elements themselves; therefore, the Pulay corrections¹⁷ are included exactly and without additional effort. The resulting forces are used in conjunction with a dynamical quenching method to search for local energy minima. In this approach the equations of motion are solved using a Gear predictor–corrector algorithm, and the resulting kinetic energy is calculated; for a maximum kinetic energy, as defined by the temperature of the system, the velocities are quenched. The process is repeated until a zero-force configuration is obtained.

Because the calculations reported here consist of materials in the condensed phase, periodic boundary conditions are used. For the integration over the Brillouin zone four special \mathbf{k} -points of the irreducible wedge are used.^{18,19} Compiler directives were

TABLE 1: Experimental Space Groups, Lattice Parameters, and Molecular Volumes for the Three Pure Crystalline Forms of HMX (α^{20} , β^{21} , and δ^{22})

phase	crystal systems	space group	lattice constants (Å)			lattice angles (°)		
			a	b	c	A	B	C
β	monoclinic	$P2_1/c$	6.54	11.05	8.70	90	124.3	90
α	orthorhombic	$Fdd2$	15.14	23.89	5.91	90	90	90
δ	hexagonal	$P6_1$ or $P6_5$	7.71	7.71	32.55	90	90	120

implemented into the electronic structure code so that calculations for the band structure energy at each special \mathbf{k} -point could be performed on a separate processor. This allows the code to run in parallel over a number of processors equivalent to the number of special \mathbf{k} -points (N_k), yielding a speed-up of approximately N_k . All calculations were performed using four processors on an SGI Origin R10000.

III. Results for the Three Pure HMX Polymorphs

In this section our first-principles electronic structure predictions for the three pure polymorphs of HMX (α , β , and δ) are presented, compared to experiment, and discussed. In addition, estimates of the bulk moduli are presented. The observed experimental structures with relevant space groups and lattice parameters^{20–22} are provided for comparison in Table 1.

We considered two levels of constraint in our calculations. In the first, which we refer to as “uniform dilation”, we fix the lattice angles to measured values for the appropriate polymorph and then increase or decrease the lattice lengths by a uniform percentage of the experimentally observed values, i.e., $a = (1 + \epsilon)a_{\text{exp}}$, $b = (1 + \epsilon)b_{\text{exp}}$, and $c = (1 + \epsilon)c_{\text{exp}}$, where $\epsilon = \pm 0.01, \pm 0.02, \dots$, etc. A complete unconstrained optimization of all atomic positions for a given set of lattice lengths and angles is then performed. This approach was applied to all three polymorphs.

For the case of β -HMX, more extensive calculations were performed using an “independent dilation” approach. In this case, the energy of the crystal was determined for a unit cell in which the lattice parameters a , b , and c were independently increased or decreased by a percentage of the experimental value, again with lattice angles fixed to experimental values. The procedure for independent dilation was implemented by cycling through sequential, independent variations in a , b , and c , with full atomic position optimization for each (a, b, c) triad. That is, a was varied for fixed values of b and c to obtain the minimum energy $E_{\min} = E_{\min}(\mathbf{q}; a, b, c)$, where \mathbf{q} denotes atomic positions. This process was repeated successively for each lattice length until the minimum energy configuration $E_{\min} = E_{\min}(\mathbf{q}; a, b, c)$ was determined. This approach has the added benefit of yielding a fairly good representation of the potential-energy surface $E = E(\mathbf{q}; a, b, c)$ in the neighborhood of the minimum. In all cases, the reciprocal lattice vectors (special \mathbf{k} -points) for the integration of the Brillouin zone were scaled according to the corresponding choice in lattice parameters a , b , and c .

Figure 2 contains plots of the calculated energies of each polymorph (total energy per atom) for several relative volumes, using the uniform dilation approach. The relative volumes shown in Figure 2 are defined with respect to the experimental volume of the β -HMX ($V_o = V_{\text{exp}}^\beta = 259.70 \text{ Å}^3/\text{molecule}$). In general, the results are of quadratic form, but the low symmetry of the structures and the imposition of constraints on the lattice angles lead to nonmonotonicity in the results. Theoretical predictions of the relative energies of the three polymorphs are provided in Table 2. We find that $E_\beta < E_\alpha < E_\delta$, in agreement with

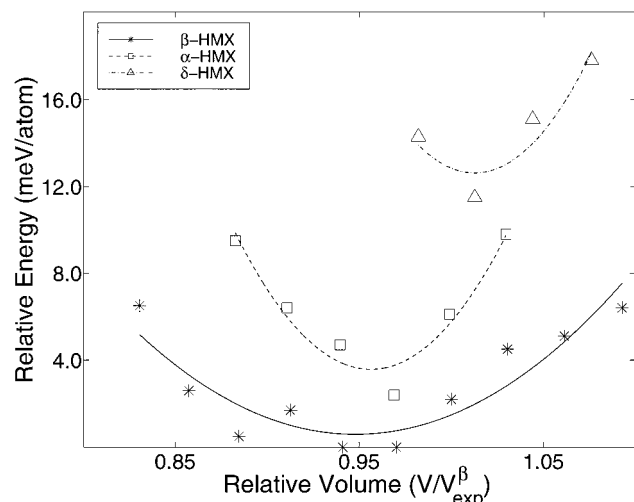


Figure 2. Energy (per atom in eV) as a function of the relative volume (with respect to the experimental volume of the individual polymorph) for the three pure crystalline forms of HMX.

TABLE 2. Theoretical Relative Energy in eV, Bulk Moduli (K_0) in GPa for the Three Pure Crystalline Forms of HMX^a

phase	E (eV/molecule)	K_0 (GPa)
β^c	0.0000	12.5
β^b	0.0648	10.2
α^b	0.1497	38.6
δ^b	0.4046	48.0

^a The relative energy is the energy per HMX molecule as measured relative to the energy of an HMX molecule in the lowest energy crystalline form (β -HMX). The bulk moduli were determined by fitting the data from the curves in Figure 2 to a parabola and then calculating the bulk moduli by $K = (1/V)(d^2E/dV^2)$. ^b For the case of uniform dilation (see text). ^c For the case of independent dilation (see text).

TABLE 3: Comparison between the Experimental and Theoretically Determined Volumes for the Three Pure Polymorphs of HMX

phase	V_{exp} (Å ³ /molecule)	V/V_{β}	V_{theor} (Å ³ /molecule)	V/V_{β}^b	relative error %
β^b	259.70	1.0000	236.92	1.0000	8.8
β^a	259.70	1.0000	246.20	1.0392	5.2
α^a	267.34	1.0294	248.36	1.0483	7.1
δ^a	279.38	1.0758	262.92	1.1097	5.9

^a For the case of uniform dilation (see text). ^b For the case of independent dilation (see text).

experiment.²³ Gas-phase calculations of the different HMX polymorphs show a similar ordering and suggest a correlation between the impact sensitivity and the total energy for these three forms.⁵

Within the uniform dilation constraint, the optimized unit cell volumes of the three pure polymorph HMX structures were calculated. These results are contained in Table 3, along with the experimentally determined volumes, and indicate reasonable agreement between experiment and theory. (Note that the results are presented as volume/molecule for ease of comparison among the polymorphs, which differ in the numbers of molecules per unit cell.) The calculated unit cell volumes are in error by 5.2%, 7.1%, and 5.9% for β -, α -, and δ -HMX, respectively, with the calculated density higher than measured in each case. The relative volumes are in fairly good agreement with experiment. The predicted independent dilation optimized β -HMX crystal parameters are $a = 0.97a_{\text{exp}}$, $b = 0.95b_{\text{exp}}$, and $c = 0.99c_{\text{exp}}$, while uniform dilation yielded lattice parameters a , b , and c that are 95% of the experimental values.

The calculated bond lengths and bond angles of the β -HMX molecules in both minimum energy structures compare favorably with the experimental structure. For the independent dilation method, the RMS deviation in bond lengths from experiment was 0.083 Å with a maximum deviation of 0.143 Å in the equatorial N–N bond length. The uniform dilation method gave an RMS bond length deviation of 0.082 Å with a maximum deviation of 0.146 Å in the equatorial N–N bond length. In addition to the results given for the bond lengths, the RMS deviation in bond angles was 3.8 (3.7) degrees with a maximum deviation of 9.3 (8.7) degrees for the independent (uniform) dilation methods. The maximum deviation is in the C–N–C angle encompassing the equatorial N–N bond.

In general, errors in the N–N bond length and C–N–C angles encompassing the equatorial N–N bond contribute significantly to a larger RMS deviation from experimental bond lengths. These relatively large deviations from experiment are attributed to the combination of using a minimal basis set as well as the LDA limit of DFT. It is expected that improvements in both levels of theory would significantly improve these N–N bond lengths. The RMS deviation from experiment is only 0.051 Å (0.052 Å for uniform dilation) when these N–N bond lengths are removed in the RMS calculation.

Calculations to yield 0 K estimates of the bulk modulus, K_0 , were performed. Specifically, the bulk modulus was approximated by fitting the results shown in Figure 2 to a parabola [i.e., $K_0 = (1/V)(d^2E/dV^2)$]. This approximation is appropriate only to the extent that the relative compressibility of the unit cell is isotropic under hydrostatic loading; otherwise, uniform dilation will result in a nondiagonal, nonuniform stress tensor rather than a simple hydrostatic pressure. The approximation is improved upon somewhat in the case of independent dilation (done for β -HMX only). However, in either instance the predicted values must be regarded as first-order estimates, due to the constrained lattice angles and use of the uniform dilation approximation.

The bulk modulus and its pressure derivative K' have been experimentally determined for room-temperature β -HMX;²⁴ the values are 13.6 GPa and 9.3, respectively. For the case of uniform dilation, our estimate for that polymorph, as recorded in Table 2 is in error by 25%. Interestingly, we predict that β -HMX has a significantly lower bulk modulus than either α - or δ -HMX, whose calculated values are 33.6 and 34.8 GPa, respectively. Unfortunately, corresponding experimental values for these polymorphs do not exist.

The bulk modulus for β -HMX for the case of independent dilation is also included in Table 2. Here, the set of points fit to quadratic form was taken to be that which defined the lower edge of the “envelope” of energies obtained in a plot analogous to Figure 2 for the entire set of (50 locally minimized) energies obtained during the independent dilation algorithm. The value obtained in this case is significantly better than that obtained for the case of uniform dilation, $K_0 = 12.5$ GPa, and is in error from experiment by 8%.

Finally, a calculation of K_0 and its pressure derivative K' was performed for β -HMX using the Murnaghan equation of state (EOS)²⁵ for the case of uniform dilation. The Murnaghan EOS is the one originally used to fit the experimental $p - V$ data.²⁴ Our predicted values, $K_0 = 12.5$ GPa and $K' = 7.5$, agree fairly well with the measured ones, $K_0 = 13.6$ GPa and $K' = 9.3$. The Murnaghan EOS was not used for the case of independent dilation due to ambiguities in how best to fit this multi-parameter function to the data.

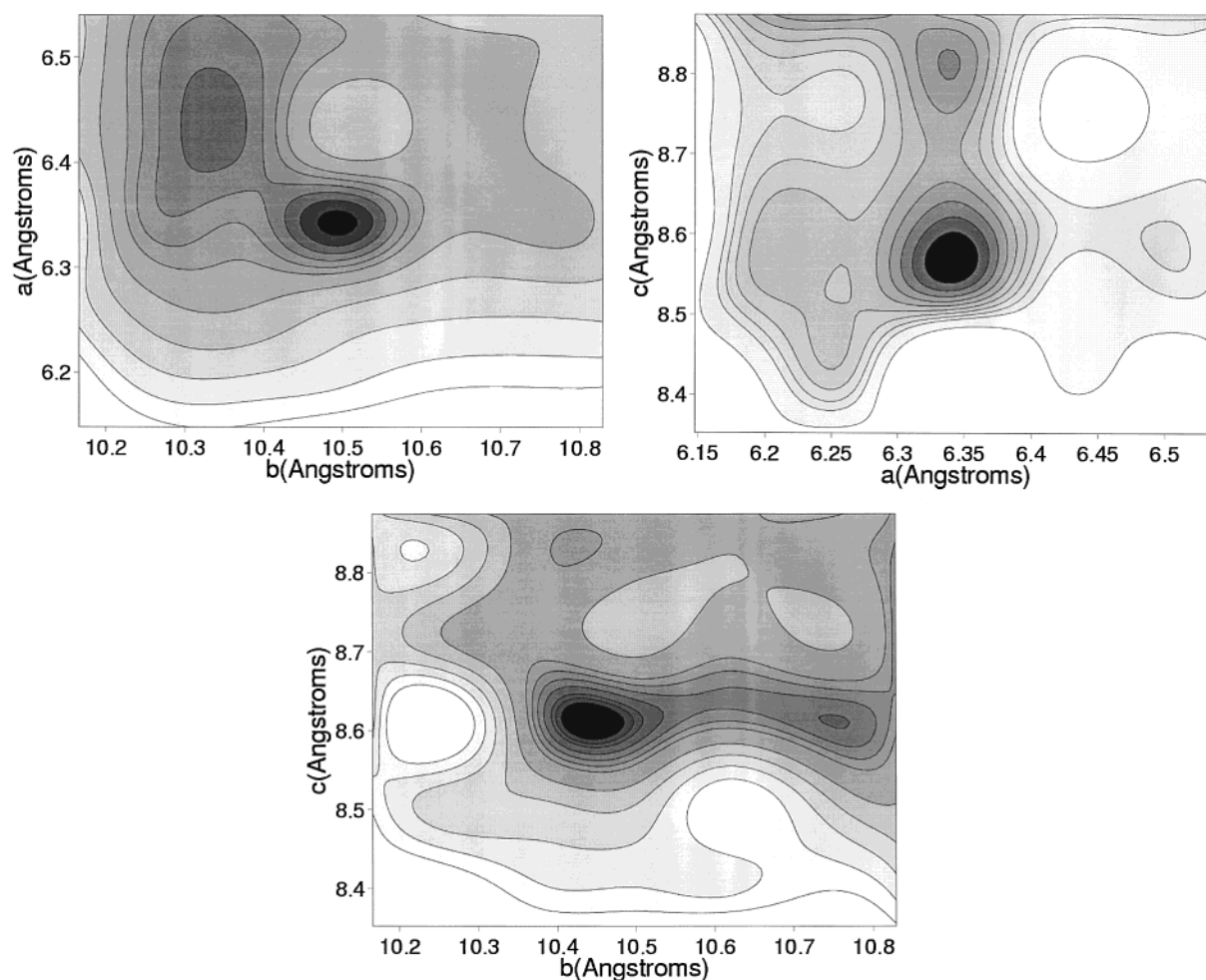


Figure 3. Contour plots demonstrating the energetics for β -HMX as a function of the lattice parameters, a , b , and c . The contour interval is 2.875 meV.

As mentioned previously, the independent dilation scheme leads to a set of geometry-minimized energies in the neighborhood of the potential energy minimum, subject only to imposition of fixed lattice angles; i.e., a potential energy surface $E = E(a, b, c)$. The results of a multidimensional interpolation of 50 minimized energy values for β -HMX are shown in Figure 3. The contour plots in Figure 3 reveal qualitative features of the energetics of β -HMX. The total energy of the unit cell rises steeply as the crystal is compressed along the direction of the c lattice parameter (panels b and c; see also Figure 1).

Closer examination of the crystal structure shows that compression along c would result in a direct interaction between the axial NO_2 groups on neighboring HMX molecules. Compression along the a axis also results in an increase in energy (panels a and b). However, compression along a results primarily in an NO_2 - CH_2 interaction that is not as spatially constrained as the NO_2 - NO_2 interaction described above. As a result, the energy contours increase with compression, but not as steeply as for compression along the c axis. Likewise, compression along the b axis (panels a and c) results primarily in an NO_2 - CH_2 interaction that is also not as spatially constrained as the NO_2 - NO_2 interaction. These interactions also carry implications for the possible condensed phase thermal decomposition mechanism of HMX, which will be the subject of a forthcoming publication.

IV. Concluding Remarks

In this paper, quantum mechanical methods were used to predict the bulk properties of the three pure crystalline phases

of HMX. Two schemes, corresponding to full geometric optimization of atomic positions with either fixed lattice angles and constant relative lattice lengths ("uniform dilation") or fixed lattice angles and independent lattice lengths ("independent dilation") were used to study the sensitivity of the results to constraints in the calculations. This work is a first step toward obtaining theoretically determinable, first-principles input which can be used for improving micromechanical simulations that are increasingly employed to aid in the development of continuum models for plastic-based explosives.

Both uniform and independent dilation were used to find optimized structures and energies for β -HMX. These yielded comparable results for the structure, bulk modulus, and pressure derivative; and the results from both methods were in reasonable accord with experiment. Optimized molecular structures, relative energetics, bulk moduli and pressure derivatives were computed for the two remaining polymorphs, within the constraints associated with uniform dilation. The predicted energetic ordering of the three phases agrees with the results of gas-phase calculations and experiment. Moreover, the present prediction of the bulk modulus and its pressure derivative obtained for β -HMX using the Murnaghan equation of state phase agrees well with experiment.

Overall, the computational method used here reasonably predicts bulk phase properties of the three phases of HMX and seems to provide a defensible description of the crystalline environment of HMX. Future work will focus on prediction of the kinetic properties of condensed phase HMX using extensions of this methodology.

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References and Notes

- (1) Gibbs, T. R.; Popolato, A., Eds. *LASL Explosive Property Data*; University of California Press: Berkeley, 1980.
- (2) Skidmore, C. B.; Phillips, D. S.; Idar, D. J.; Son, S. F. In *Conference Proceedings: Europyro 99 Vol. I*, Association Francaise de Pyrotechnie: Brest, 1999; 2.
- (3) Idar, D. J.; Lucht, R. A.; Straight, J. W.; Scammon, R. J.; Browning, R. V.; Middleditch, J.; Dienes, J. K.; Skidmore, C. B.; Buntain, G. A. In *Proceedings of the Eleventh International Detonation Symposium*; Snowmass Village, CO, Aug 31 – Sept 4, 1999; Naval Surface Warfare Center: Indian Head, 1999; 335.
- (4) Melius, C. F.; Binkley, J. S. In *Twenty-first Symposium (International) on Combustion*; The Combustion Institute, 1986; 1953. Melius, C. F. In *Chemistry and Physics of Energetic Materials*; Bulusu, S. N., Ed.; Kluwer Academic Publishers: Norwell, MA, 1989; 21.
- (5) Kohno, Y.; Maekawa, K.; Tsuchioka, T.; Hashizume, T.; Imamura, A. *Chem. Phys. Lett.* **1993**, 214, 603. Kohno, Y.; Maekawa, K.; Tsuchioka, T.; Hashizume, T.; Imamura, A. *Combust. Flame* **1994**, 96, 343.
- (6) Harris, N. J.; Lammertsma, K. *J. Am. Chem. Soc.* **1997**, 119, 6583.
- (7) Wu, C. J.; Fried, L. E. *J. Phys. Chem. A* **1997**, 101, 8675.
- (8) Rice, B. M.; Chabalowski, C. F. *J. Phys. Chem. A* **1997**, 101, 8720.
- (9) Kuklja, M. M.; Kunz, A. B. In *Shock Compression Conference Proceedings UT*, 1999; in press.
- (10) Hamann, D. R.; Schliiter, M.; Chiang, C. *Phys. Rev. Lett.* **1979**, 43, 1494.
- (11) Bachelet, G. B.; Hamann, D. R.; Schliiter, M. *Phys. Rev. B* **1982**, 26, 4199.
- (12) Harris, J. *Phys. Rev. B* **1985**, 31, 1770.
- (13) Sankey, O. F.; Niklewski, D. J. *Phys. Rev. B* **1989**, 40, 3979.
- (14) Sankey, O. F.; Demkov, A. A.; Windl, W.; Fritsch, J. H.; Lewis, J. P.; Fuentes-Cabrera, M. *Int. J. Quantum Chem.* **1998**, 69, 327.
- (15) Demkov, A. A.; Ortega, J.; Sankey, O. F.; Grumbach, M. P. *Phys. Rev. B* **1995**, 52, 1618.
- (16) Hellmann, H. *Einführung in die Quantumchemie*; Franz Duetsche: Leipzig, 1937. Feynman, R. P. *Phys. Rev.* **1939**, 56, 340.
- (17) Pulay, P. *Theor. Chim. Acta* **1979**, 50, 299.
- (18) Chadi, D. J.; Cohen, M. L. *Phys. Rev. B* **1973**, 8, 5747.
- (19) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, 13, 5188.
- (20) Cady, H. H.; Larson, A. C.; Cromner, D. T. *Acta Crystallogr.* **1963**, 16, 617.
- (21) Choi, C. S.; Boutin, H. P. *Acta Crystallogr. B* **1970**, 26, 1235.
- (22) Cobbleddick, R. E.; Small, R. W. H. *Acta Crystallogr. B* **1974**, 30, 1918.
- (23) McCrone, W. C. In *Physics and Chemistry of the Organic Solid State*; Fox, D.; Labes, M. M.; Weissberger, A., Eds.; Wiley: New York, 1965; 725; Vol. II.
- (24) Olinger, B.; Roof, B.; Cady, H. In *Actes du Symposium International sur le Comportement des Milieux Denses Sous Hautes Pressions Dynamiques*; Editions du Commissariat al'Energie Atomique, Centre d'Etudes Nucleaires de Sarclay: Paris, 1978; 3.
- (25) Murnaghan, F. D. *Finite Deformation of an Elastic Solid*; Wiley: New York, 1951.